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1. Introduction

The electroanalysis has revealed that there is a huge application field for the researches that involve the nanostructured and multilayer electrode interfaces. Nevertheless, even a simpler approach as the anodic electrode activation, can be used with success to improve the detection of organic compounds at very low concentration levels. Several research papers report on the application of electrochemical methods for the quantification of drugs, and in the last ten years the use of carbon electrodes in this field has considerably increased [1].

2. Relation

In this work, inserted in a project funded by the Compagnia di San Paolo and by the Turin University, we studied and optimized a simpler approach for acetaminophen determination at trace levels using a bare GCE, exploiting an electrochemical activation procedure. We observed that exposing a GCE to a high potential (2 V vs Ag/AgCl) for a limited period (60s) in presence of 50 mM borate/phosphate buffer (hereinafter BPB, pH = 9) a strongly electro-active layer is formed. The activated layer has been characterized by means of electrochemistry (CV), Raman spectroscopy, electron microscopy and X-ray photoelectron spectroscopy (XPS) in order to understand its nature. Then the activated electrode has been exploited in the electroanalysis of the acetaminophen (AP) by differential pulse voltammetry (DPV).

2.1 Activated GCE characterization

The activated surface area is almost the same of the bare electrode, from 5.5 to $5.1 \cdot 10^{-6}$ m^2 and the surface maintains a mirror-finished electrode surface without evident morphologic damage to the naked eye. The chronoamperometric (CA) response of the electrode showed a characteristic current increase few seconds later than the zeroing of the capacitive current contribution; the CA current after reaching a plateau was stable even after several measurements. Such behaviour seemed to suggest the onset of a chemical reaction that allowed the formation of a finite number of polar groups on the surface that increased the electrical conductivity. Interestingly, the CA response and the consequent electroanalytical performance, appeared to be strongly dependent on the choice of the anodizing electrolyte. High currents for the AP measurement were observed only when the phosphate or borate anions were used as anodizing electrolyte. The cyclic voltammetry at reducing potential, after the anodization in the presence of BPB as electrolyte, showed a huge increase of the cathodic current at very low potential (-1.8 and -2.1 V vs Ag/AgCl/NaCl sat). Much lower intensity was observed when KCl 0.1 M pH 9 was used as anodizing electrolyte. The effect of the activation on the electrochemical probe $K_3Fe(CN)_6$ is evident in terms of acceleration of the electron transfer: in fact a decrease of ΔEp from 181 to 111 mV was measured (ΔEp= Epa-Epc). In the Raman spectra, the bands at ~1330 and ~1600 cm^{-1} correspond to D and G modes, respectively; a decrease in the D/G band ratio from 1.63 to 1.37 is revealed upon activation, that means a reduction in the

defectivity degree of the surface [2], and it could be explained as the formation of a compact and homogeneous coverage. XPS spectra showed a massive increase of oxygen bound to the electrode surface after the activation, with an abundance that pass from 6 to 30%; deconvolution of the spectrum demonstrates that the oxygenated functions are mainly phenolic and carbonyl groups. SEM images showed a perfectly smooth surface, only slightly more conductive than the original surface; magnification up to 240000x did not give more information. Analogously, also the analysis of the AFM images showed only a slightly lower roughness of the material surface after activation.

2.2 Analytical method optimization

The activated electrode has been exploited in the electroanalysis of the paracetamol (DPV). In this application, beside the first activation in the blank solution, a very short anodic treatment time (5s, 2V vs Ag/AgCl) has showed to be helpful in improving the analytical performance of the electrode: LoD $2 \cdot 10^{-9}$ M, LoQ $9 \cdot 10^{-9}$ M in borate/phosphate buffer. Interestingly both the pre-treatment in the blank solution and the anodization step in sample appear to be correlated to the sensitivity of the system and only the electrodes that underwent both the activations reached the LoD above reported. The effect of the anodic activation on the electrochemistry of AP appeared to be correlated to an improved electron transfer kinetics and a better reversibility of the electrochemical oxidation. Interestingly, the analyte signal did not show at the first DPV scan, but at least 10 scans were necessary before obtaining a maximum and stable result. It appear that the background decrease during the series of DPV, yielding a measurable analyte signal. Such singular behaviour could be related to a slow diffusion of AP through the electrode-solution porous layer created during the activation.

3. Conclusions

The activation of the GCE caused a dramatic improvement of the LoD and LoQ values, and our procedure compares very well with other voltammetric methods based on chemically modified electrodes [3-5]. Moreover our method could be capable of detecting AP at concentration known to be present in water samples that ranges between 1 and 10 µg/L.

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